A porphyrin-based gelator assembly which is reinforced by peripheral urea groups and chirally twisted by chiral urea additives

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Abstract—A novel porphyrin (**1b**) bearing four urea groups at its periphery was synthesized. This compound tends to aggregate into one-dimensional direction, resulting in an organogel phase in anisole and diphenyl ether solvents. The gel can be formed even at 0.125 wt/vol% in anisole and the sol-gel phase transition temperatures (T_{gel}) are as high as 120–140°C, indicating that **1b** acts as an excellent gelator for these specific solvents. The spectroscopic studies and electron-micrographic observations support the view that the π–π stacking interaction among porphyrin moieties and the hydrogen-bonding interaction among urea moieties operate synergistically to give rise to a stable one-dimensional aggregate structure indispensable for gel formation. Further interestingly, chiral urea derivatives are bound to this aggregate to twist it in a chiral manner. This is a unique example for a rationally-designed organogelator including a porphyrin core and urea peripheral groups. © 2002 Elsevier Science Ltd. All rights reserved.

It is well-known that porphyrins and phthalocyanines tend to align into one-dimensional aggregates and therefore are of much concern in relation to creation of novel supramolecular architectures such as nanowires, discotic liquid crystals, helical ribbon structures, etc.[1–5] The major driving force in these architectures is considered to be π–π stacking and/or van der Waals interactions. More recently, another supramolecular architectures constructed in organogels attracts the broad attention of supramolecular chemists: the origin of organogel formation is considered to be one-dimensional alignment of gelator molecules supported by these interactions and/or hydrogen-bonding interactions.[6,7] This situation has offered a new idea that porphyrins and phthalocyanines, which a priori tend to assemble into the one-dimensional supramolecular structure, would act as a powerful aggregative core for the design of new gelators. In addition, we have found that many new hydrogen-bond-based gelators can be developed utilizing a natural library of carbohydrate molecules.[8–10] The finding suggests that one-dimensional aggregates comprised of porphyrins or phthalocyanines would be 'reinforced' by the hydrogen-bonding interaction among saccharide groups covalently-appended to the central porphyrin (or

phthalocyanine) column. However, this idea has scarcely been utilized for the design of a robust organogel system.[11] With these objects in mind we previously synthesized porphyrin **1a** bearing four peripheral β-D-galactopyranoside groups.[12] We found that **1a** results in stable organogels showing both thermotropic and lyotropic behaviors.[12] Another potential building block to construct a stable one-dimensional motif is a urea group.[7a,13] It thus occurred to us that **1b** bearing four peripheral urea groups would act as another versatile organogelator. We have found that **1b** results in very stable organogels with T_{gel} (sol-gel phase transition temperature) >140°C and further interestingly, the formed fibrous aggregate can be chirally twisted by addition of chiral urea derivatives.

1a; R=

1b; R=
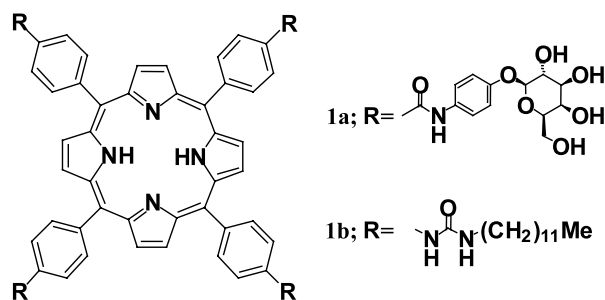
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Compound **1b** was synthesized by the reaction of 5,10,15,20-tetrakis(4-amino-1-phenyl)porphyrin and dodecyl isocyanate in THF. The product (**1b**: mp> 270°C (dec.)) was identified by ^{1}H NMR and MALDI-TOF-MS ([M+H][+] 1521.17) spectral evidence and elemental analysis. The gelation test was carried out as follows: **1b** was dispersed in solvent (1.0 wt/vol%: 6.6 mM) and the mixture was heated in a septum-capped test tube. The solution was cooled to room temperature and left for one day in the dark. By this treatment, **1b** was insoluble in most solvents (water, methanol, ethanol, acetone, THF, ethyl acetate, decaline, etc.), but
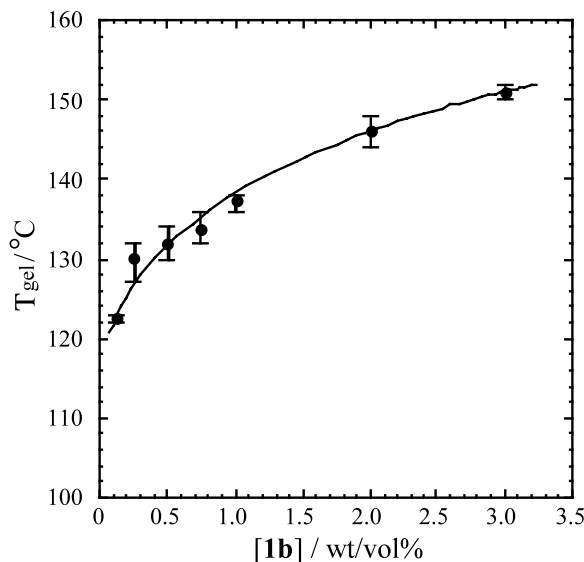

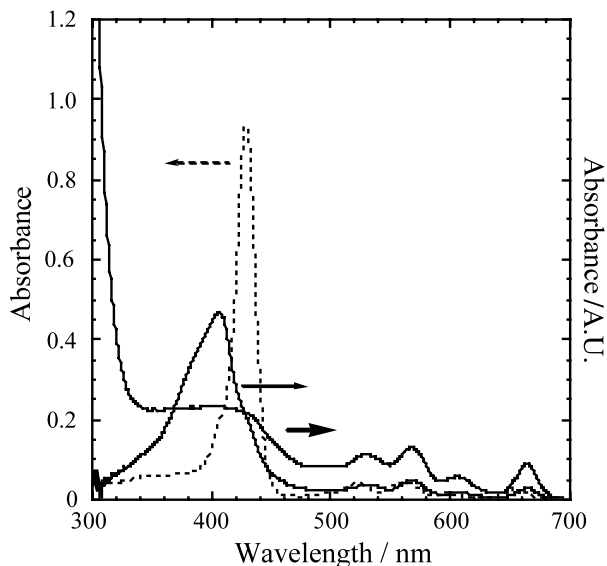**Figure 1.** Plot of T_{gel} against gelator concentration in anisole.

Figure 2. UV–vis absorption spectra in homogeneous CHCl$_3$:DMSO = 1:1 solution (broken line; [**1b**] = 0.1 mM, 1 mm cell), anisole gel (thin line; [**1b**] = 0.5 wt/vol% (3.3 mM)), and that with (S)-**2** (bold line; [(S)-**2**] = 13.2 mM) at 25°C; the gel phase spectra were measured with a sample sandwiched by two glass plates, so that the ordinate is arbitrary unit; the spectrum with (R)-**2** is the same as that with (S)-**2**.

specifically gelated anisole and diphenyl ether. Thus, we evaluated the gelation ability in anisole.

The 'stability' of organogels is usually evaluated with two factors, viz., critical gelation concentration (CGC) where the sol phase changes into the gel phase and sol-gel phase transfer temperature (T_{gel}) where the gel melts into the sol solution.[7] The T_{gel} values were determined in anisole as a function of gelator concentration (Fig. 1). It is seen from Fig. 1 that the CGC for **1b** is very low (0.125 wt/vol%) and the T_{gel} is as high as 130°C even at [**1b**] = 0.25 wt/vol% (1.7 mM). The T_{gel} values increase further with increasing **1b** concentration and reach 150°C at [**1b**] = 3.0 wt/vol% (19.8 mM). The results indicate that **1b**, which is rationally designed so that the one-dimensional supramolecular structure can be formed by the synergistic effect of porphyrin–porphyrin π–π stacking and urea–urea hydrogen-bonding interactions, can act as an excellent gelater showing both the very low CGC and the very high T_{gel}.

Direct evidence for the porphyrin–porphyrin stacking was obtained from UV–vis absorption spectral examinations. As shown in Fig. 2, **1b** in homogeneous anisole solution gave a Soret band at 429 nm and Q bands at 522, 561, 596, and 654 nm. In the gel phase, the sharp Soret band shifted to shorter wavelength (404 nm) with the significant broadening of the peak. This blue shift implies that the porphyrin moieties form a stacked aggregate.[14] The Q bands in the gel phase appeared at 530, 567, 607, and 664 nm, which were all red-shifted compared with those in homogeneous solution. The red shift is also compatible with the formation of porphyrin–porphyrin stacked aggregates.[14] To obtain a visual insight into the aggregation mode, scanning electron microscopy (SEM) pictures were taken of a xerogel of **1b** in anisole. As shown in Fig. 3, one can recognize a well-developed network structure consisting of fibrils with diameters of 100∼300 nm.

The foregoing results consistently support the view that in the gel fibrils of **1b** the porphyrin moieties assemble
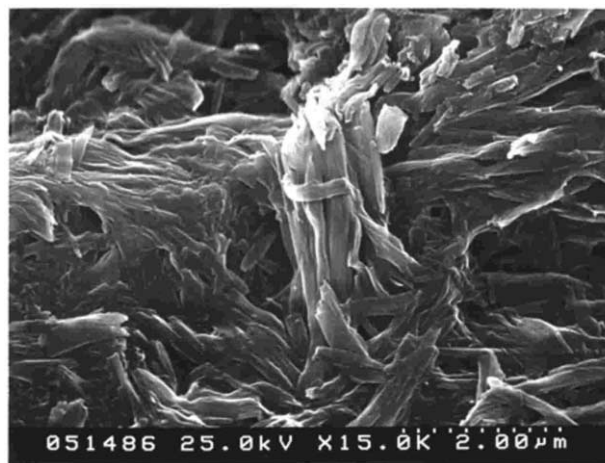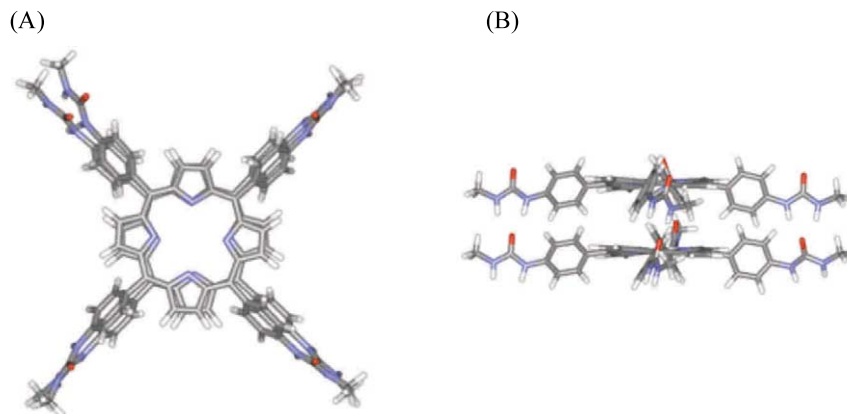

Figure 3. SEM picture of a xerogel obtained from **1b** gel (2.0 wt/vol% in anisole).

(A) (B)

Supplementary Figure 1. Energy-minimized structures of **1b** in the absence of **2** with Discover 3/Insight II 98.0; (A) top view, (B) side view. In the computational process, the distance between nitrogen and oxygen in the urea groups was fixed to 2.9 Å which was generally obtained from the crystal data of urea compounds.

(A) (B)
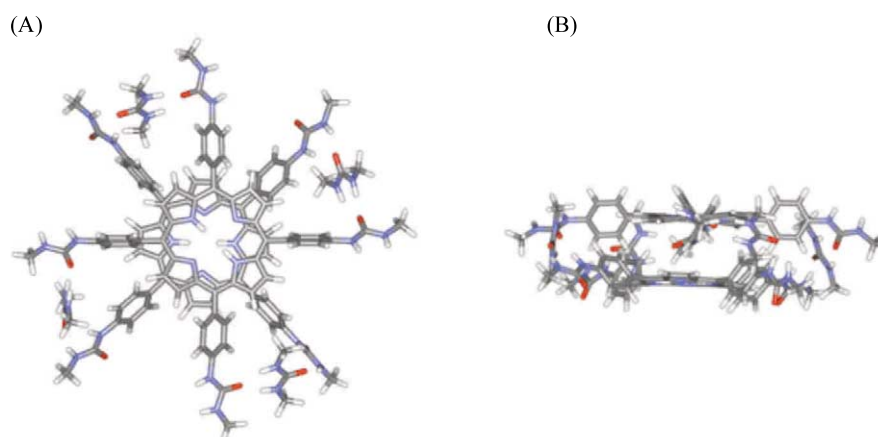
Supplementary Figure 2. Energy-minimized structures of **1b**: *N,N′*-dimethyl urea = 2:4 complex with Discover 3/Insight II 98.0; (A) top view, (B) side view. The assumption used for this calculation is described in a caption to Supplementary Figure 1.

into a one-dimensional aggregate in a face-to-face manner. As the organogel fibrils partially have a character of the solid state,[15] one may simulate the aggregation mode with that in the solid state. When two **1b** molecules aggregate using the urea–urea hydrogen-bonding interactions, the porphyrin–porphyrin distance in the energy-minimized structure is estimated to be 0.488 nm (Supplementary Figure 1S). The result is very reasonable because the value is in the midst of that of porphyrins without *meso*-substituents (0.36 nm) and that of tetraphenylprophyrins (0.65 nm).[14] When the urea–urea distance is elongated by the rotation of the porphyrin rings, four *N,N′*-dimethylurea can complementarily fit this clefts (Supplementary Figure 2S). In this complex, the porphyrin–porphyrin distance is still kept to a realistic one, 0.440 nm, indicating that the urea guest binding is feasible. This means that when some appropriate urea derivative is added, it may be inserted into the hydrogen-bonding urea align in the one-dimensional porphyrin stack. Taking this information into account, we added (*R*)- and (*S*)-enantiomers of *N*-(1-phenylethyl)-*N′*-dodecyl urea ((*R*)-**2** and (*S*)-**2**, respectively) to the gel system. As shown in Fig. 2, the UV–vis spectrum of the gel was significantly broadened, suggesting that the porphyrin–porphyrin stacking

is further intensified by addition of (*S*)-**2** (or (*R*)-**2**).[14b,c] The complementary result on the effect of (*S*)-**2** addition was also obtained from T_{gel}: as shown in Fig. 4,
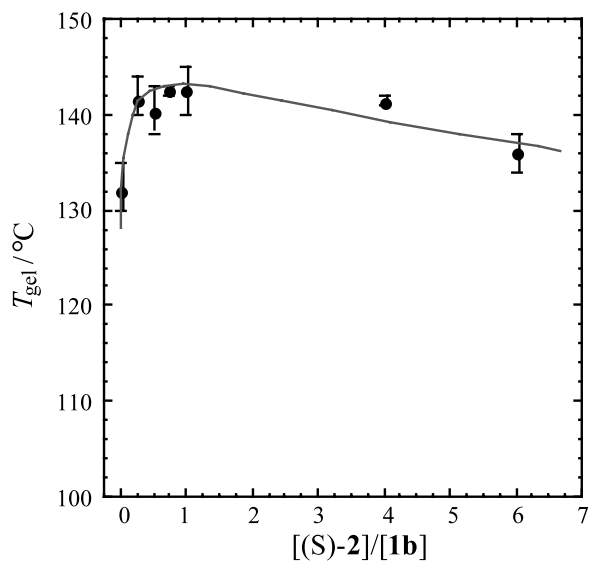
Figure 4. Influence of added (*S*)-**2** on the T_{gel}: [**1b**] = 0.25 wt/vol% (1.7 mM).
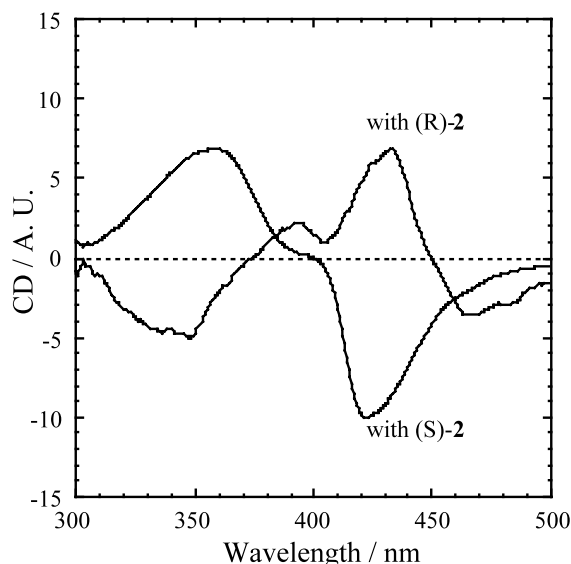
Figure 5. CD spectra of **1b** (0.5 wt/vol%; 3.3 mM) in the presence of **2** (13.2 mM) in the gel phase at 25°C; the spectra were measured with a sample sandwiched by two glass plates, so that the ordinate is arbitrary unit.

the T_{gel} values are initially enhanced by (S)-**2** addition and then gradually decreased. This dependence implies that the porphyrin–porphyrin stacking is further stabilized by bound (S)-**2** at [(S)-**2**]/[**1b**] = 0.6 ~ 1.0.

Here, it occurred to us that bound (S)-**2** (or (R)-**2**) might generate a driving force to chirally twist the one-dimensional porphyrin stack. This idea can be examined by circular dichroism (CD) spectroscopy. As shown in Fig. 5, added (S)-**2** induces the negative exciton-coupling band whereas added (R)-**2** induces, nearly symmetrically to that with (S)-**2**, the positive exciton-coupling band. Under the same measurement conditions, the linear dichroism (LD) spectra were negligibly small. One can thus regard that the one-dimensional porphyrin stack is chirally twisted by bound chiral urea derivatives (as shown in the graphical abstract).

In conclusion, the present paper has demonstrated that a urea-appended porphyrin derivative, which is rationally designed toward construction of one-dimensional aggregates, acts as an excellent gelator for very specific solvents. Although one-dimensional alignment of porphyrins has been attained in liquid crystal systems[1] and crystal systems,[2] such a precedent scarcely exists in an organogel system.[12] The organogel system, being different from the liquid crystal and crystal systems, can feature both thermotropic and lyotropic characters, which are conveniently used to append the switch function and the self-assembling function to the one-dimensional porphyrin stack. In fact, the present preliminary study has shown that added urea derivatives can change the nature of this one-dimensional porphyrin stack. We therefore believe that these functional variations possible in the organogel phase are useful to control the catalytic and photochemical functions of porphyrins existing as a core of the one-dimensional array.

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